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Abstract

Three upland Lake District Tarns, Scoat, Greendale and Burnmoor, have been evaluated using MAGIC (Model of Acidification of Groundwater In Catchments) to reconstruct past, present and future chemical behaviour. The modelled historical changes in acidity are compared with palaeoecological estimation of pH to demonstrate model validity. Chemistry as simulated for all anions and cations and two of the three lakes are shown to have undergone significant acidification. The effects of changing atmospheric pollution levels on lake chemistry is evaluated and 80–90% sulphur reduction levels are required to achieve zero alkalinity. The impacts of increased nitrogen deposition are assessed and are shown to further delay reversibility.

Introduction

Acidification is a continuing problem in upland Britain where high loadings of oxides of sulphur and nitrogen impact thin base–poor soils and create acid conditions. There have been significant developments in understanding the processes controlling acidification, particularly as a result of the Royal Society Surface Waters Acidification Programme (Mason, 1990) and pioneering research in Scotland (Harrison and Morrison, 1982). Catchment studies across the UK have provided data for process studies and modelling of acidification trends. Jenkins *et al.* (1990a, b) and Whitehead *et al.* (1988a, b, 1993) applied models to catchments in England, Scotland and Wales and Wright *et al.* (1990) and Cosby *et al.* (1985a, b) simulated behaviour in catchments in Norway and North America.

The Lake District in the UK is an area receiving high loadings of acidic deposition and has a geology which is susceptible to acidification (Kinniburgh and Edmunds, 1986). In this paper three upland tarns (see Figure 1) have been studied to investigate trends in acidification, explore critical loads and to assess the potential for reversibility and investigate the impact of nitrogen on upland acidification.

The MAGIC Model

The MAGIC (Model Acidification of Groundwater in Catchments) model developed by Cosby *et al.* (1985a, b), has been explicitly designed to perform long term simulations of changes in soil water and stream water chemistry, in response to changes in atmospheric acidic deposition. The model is based on the assumption that surface-water chemistry is determined by reactions taking place in the soils within the catchment.

The model includes terms describing the important phenomena controlling a system's chemical response to acid deposition, yet is restricted in complexity so that it can be implemented on diverse systems with a minimum of *a priori* data. It is a physically-based conceptual model, using lumped representation of the spatially distributed catchment processes. The model is based on the mathematical representation of the processes thought to be the primary catchment controls on acidification namely:

1. Anion retention of catchment soils (eg. sulphate adsorption)
2. Adsorption and exchange of base cations and aluminium in soils
3. Alkalinity generation by dissociation of carbonic acid at high CO_2 partial pressures in the soil, with subsequent exchange of hydrogen ions for base cations
4. Control of Al concentration by an assumed equilibrium with a solid phase of $Al(OH)_3$
5. Weathering of minerals in the soil to provide a source of base cations
6. The key driving factor in MAGIC is the deposition of oxides of sulphur and other inputs over long periods of time (see Figure 2)

The MAGIC model simulates these processes by using:

1. a set of equilibrium equations which quantitatively describe the equilibrium soil processes and the chemical changes that occur as soil water enters the stream channel.
2. a set of mass balance equations which quantitatively describe the catchment input/output relationship for base cations and strong acid anions in precipitation and stream water.
3. a set of definitions which relate the variables in the equilibrium equations to the variables in the mass balance equations.

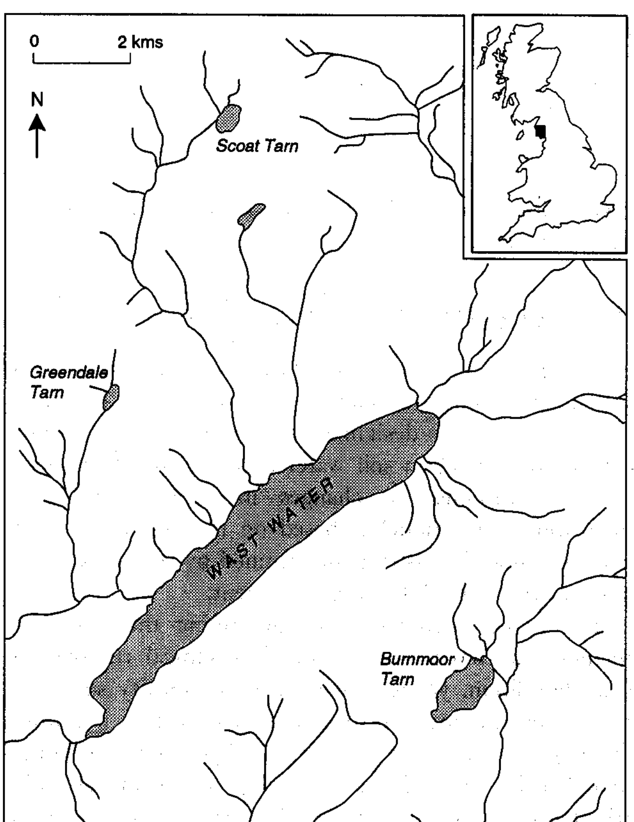

Fig. 1 *Location of the study sites in the western Lake District*

The model has its roots in the Reuss Johnson conceptual system (Reuss and Johnson 1985) but it has been expanded from a two component Ca-Al system to include other important cations present in catchment soils. The chemical conditions in the soil are assumed to be uniform throughout the depth considered and the vertical stratification of soils is assumed to be unimportant. These assumptions are probably too overly restrictive for short term water quality response but, for use in long term average water quality studies, it is more valid. Many of the dynamic quality changes arising from spatial heterogeneity disappear into slower long term changes, which are determined by single bulk properties of the whole catchment (Cosby *et al.*, 1985a, b)

The Lake District Tarns

Of the three tarns studied, two are very acidic, Scoat Tarn and Greendale Tarn and one is only slightly acidic, Burnmoor Tarn. The tarns are close to each other in the Wasdale/Eskdale area (see Figure 1).

The catchments that drain into the tarns are treeless moorlands characterised by rough grasses and mosses, with the land use confined to low intensity sheep grazing. The bedrock of the catchments is igneous Ordovician of the Borrowdale Volcanic series, which is slow weathering. The major ions which are made available by weathering bedrock, are Ca^{2+}, Mg^{2+} and some Na^{+}, with K^{+} derived chiefly as input from precipitation (Sutcliffe and Carrick 1983). Scoat Tarn is a small deep corrie tarn, in a west facing valley with steeply sloping walls surrounding the lake and represents a glacial source area during the most recent part of the Pleistocene glaciations. Bare rock covers 29% of the catchment with the eastern slopes mainly rock and boulders, while those to the north and south are less steep and covered with rough grass and sphagnum. Two small streams drain into the tarn from the catchment and the outflow from the western corner flows into Wastwater via Nether Beck. The littoral area of the lake is composed of gravels, bedrock and boulder scree. Burnmoor Tarn is the largest upland lake in the English Lake District and occupies the saddle area between areas of high ground. It probably served as a through route for ice during the glaciations and substantial deposits of glacial till are present around the tarn, which results in the catchment having a comparatively high base saturation for its bedrock geology. There are four main inflow streams to the north and northwest, with the outflow at the eastern end immediately joining the Hardrigg Beck, which drains the slopes of Scafell. Greendale is intermediate between Burnmoor Tarn and Scoat Tarn in terms of glacial origin, having

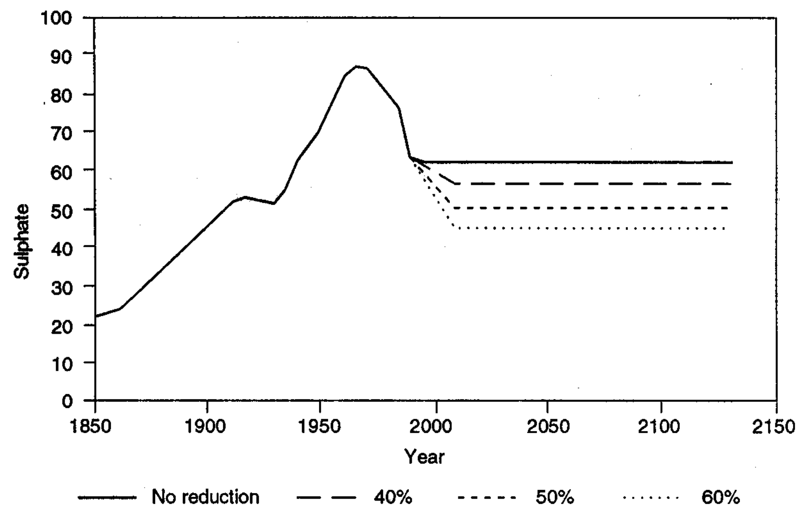

Fig. 2 *Sulphate deposition trajectory used with the MAGIC simulation*

both areas of scree and bare rock as well as till deposits. Information on Tarn characteristics is given in Table 1.

Table 1. Summary Lake statistics

	Scoat Tarn	Burnmoor Tarn	Greendale Tarn
Estimated Rainfall (myr^{-1})	3.30	2.10	3.30
Estimated Discharge(myr^{-1})	2.77	1.76	2.77
Lake Area (ha)	5.20	24.00	2.10
Volume ($m^3 \times 106$)	0.42	0.89	0.20
Catchment Area (ha)	92	226	89
Tot vol in (m^3yr^{-1})	330.6	525.0	280.8
Retention Time (yr)	0.13	0.17	0.07

The fish population of Scoat Tarn is small and electrofishing at the outflow in 1989 produced only three trout (UKAWMN 1991). There are similarly poor fish stocks at Burnmoor Tarn where electrofishing in 1989 produced a minimum density of 0.016 fish m^{-2}.

Palaeolimnological record

The historical pH change derived from the diatom reconstruction of a sediment core at Scoat Tarn shows a very marked decline of planktonic species. There is a decrease in the circumneutral species being replaced mainly by the acidophilous species and acidobiontic taxa especially in the more recent, post-1850, sediment. The Index B pH reconstruction indicates that there has been a decrease, from 6.1 at the base of the core to 4.6 in 1985. The historical pH values can be seen in Fig. 3 along with the error bounds of the diatom analysis of +0.3 pH units (Haworth 1985, Haworth *et al.* 1988). The main acidification dates from about 1850 and analysis of zinc and magnetic minerals in the core (Haworth 1993), which are indicative of atmospheric contamination, shows increased atmospheric contamination. At Greendale Tarn the acidification was also confirmed by Haworth (1993) who identified the expansion of the more acid tolerant taxa as the pH decreased after about 1900.

The palaeoliminological record of diatom assemblages in the sediment at Burnmoor Tarn (Haworth *et al.* 1987), show little indication of change or evidence of recent acidification experienced at other tarns, despite the influx of atmospheric pollutants. The diatom-reconstructed pH remains constant at about 6.2; however, there are changes in the proportions of plankton taxa in post-1850 sediments, suggesting a very slight shift to a more acid flora over the last 100 years. Clearly the loss of alkalinity has not been sufficient to cause a significant change in pH. The historical pattern and intensity of acid deposition will be similar for each site and so the different response of the catchments is clearly influenced by the difference in their neutralising capacity.

Rainfall, soil and tarn chemistry

The rainfall chemistry used as an input to the MAGIC model is from Ennerdale, 4km north west of Scoat Tarn which is the same distance from the sea and therefore, can be assumed to receive the same sea influence as that of Scoat Tarn. The catchment is in a very wet part of the country with Scoat Tarn receiving an estimated annual rainfall of 3300mm whilst Burnmoor Tarn receives a lower annual rainfall total of 2100 mm (see Table 1).

The volume-weighted mean annual concentration of the rainfall chemistry is given in Table 2 for the period 1982–1990.

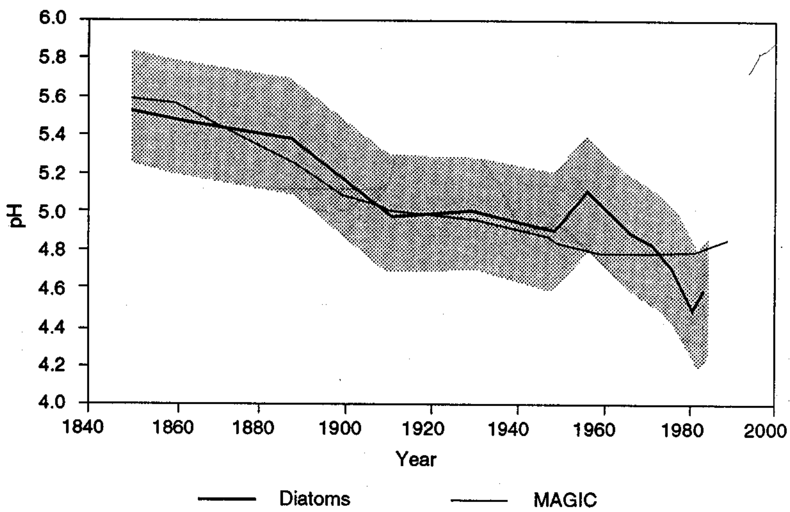

Fig. 3 *Scoat Tarn MAGIC and diatom pH values*

Table 2. Weighted Average Bulk Precipitation Chemistry for Ennerdale (all units μeq l^{-1} except pH)

	pH	H^+	Na	Mg	K	Ca	NH_4	Cl	NO_3	SO_4
1982	4.7	20.0	195.0	46.0	5.0	13.0	13.0	241.0	8.0	43.0
1983	4.8	19.3	134.1	33.0	6.1	35.9	22.9	171.4	23.9	45.2
1984	4.7	28.1	130.6	33.2	5.0	33.4	26.9	163.1	28.4	55.6
1985	4.9	17.6	80.1	21.1	2.5	26.7	23.1	197.1	20.6	41.1
1986	4.9	19.2	149.7	34.8	3.4	25.0	23.5	176.7	23.4	45.5
1987	4.8	21.0	86.5	20.1	2.2	22.9	20.6	102.9	22.1	38.7
1988	4.8	16.0	117.0	28.0	2.0	8.0	12.0	134.0	10.0	37.0
1989	4.8	16.4	121.0	28.0	3.0	22.3	11.0	133.8	16.2	44.6
1990	4.7	21.2	228.3	53.1	5.5	22.3	17.8	283.4	20.3	59.5

The Lake District is a maritime region and the rainwater contains relatively large quantities of sodium and chloride ions. The rainfall chemistry is characterised by large concentrations of calcium, sulphate, nitrate and ammonium ions, far in excess of marine origins, indicating the considerable anthropogenic deposition in the area. Excess calcium in the bulk deposition relative to that of sea water concentration has been recorded before (Sutcliffe *et al* 1982) and is probably derived from wind blown dust from the south and east (Gorham 1958). The rainfall collector is at an altitude of 112m, but the catchments under study are at a much higher altitude. Deposition has been shown to differ with altitude (Fowler *et al.* 1988) and therefore there could be significant differences in the composition of bulk deposition received from that measured, as a result of orographic cloud.

Soil surveys were made of the catchments to provide information on soil characteristics for the model. A summary of the soil chemistry can be seen in Table 3.

Table 3. Soil Characteristics—weighted averages

	Scoat	Greendale	Burnmoor
CEC meq kg^{-1}	197.1	246.9	219.5
Na %	1.1	1.5	1.6
K %	0.8	1.1	1.2
Ca %	3.8	7.2	12.7
Mg %	3.1	5.4	5.5
Al %	91.1	84.7	78.9
Base Sat %	8.8	15.3	21.1

Three major soil types were encountered in the catchments, rankers, peats and podzolic soils. The rankers are shallow soils with rock within 40 cm of the surface while the peats have poor hydraulic conductivity; therefore neither play a large part in neutralising acidity. In contrast, the podzolic soils are developed mainly in thick deposits of glacial till which will be a richer source of cations for neutralisation. At Scoat Tarn, podzolic soils are located well back from the shore and hence are not able to neutralize much of the water that enters the tarn. Burnmoor Tarn has the greatest proportion of podzolic soils compared to the other two sites and these are located both adjacent to the tarn shore and in the source areas of inflowing becks; therefore soil water from the peats and rankers could be neutralised by the buffer rich soils before entering the tarn.

The water chemistry of all three tarns has been measured as part of the United Kingdom Acid Waters Monitoring Group (UKAWMG) Study. Lake chemistry data are also available from previous studies by the Freshwater Biological Association from 1953. Sutcliffe *et al*

(1982) compared the chemical composition of tarn waters and concluded that there was no evidence that the pH of low alkalinity, unproductive lakes in the Lake District had decreased over a period of 50 years but that the change in acidity dated from the mid 1850s at the height of the industrial revolution. A summary of the chemistry data is shown in Table 4 and indicates highly acid waters in Scoat and Greendale Tarns compared with the well buffered water of Burnmoor Tarn. The Burnmoor Tarn water has a much higher calcium concentration indicating a significant source of calcite weathering within the catchment derived from the glacial till. This calcium provides the source of cations to maintain a pH of 6.5 in Burnmoor compared to 4.9 in Scoat and 5.2 in Greendale.

Table 4. Chemistry of Scoat, Greendale and Burnmoor Tarns (all units $\mu g l^{-1}$ except pH)

	Scoat	Greendale	Burnmoor
Ca	35.7	53.0	95.8
Mg	50.6	62.0	68.9
Na	178.3	188.0	208.5
K	8.7	6.0	6.1
SO_4	60.7	85.0	81.4
Cl	206.6	209.0	233.6
pH	4.93	5.2	6.5

Table 5. Scoat Tarn parameter values

SO_4^{2}-adsorption half saturation ($meqm^{-3}$)	200
SO_4^{2}-adsorption maximum capacity ($meqkg^{-1}$)	1
Solubility $Al(OH)_3$	7.5
Selectivity coefficient A/Ca	1.23
Selectivity coefficient A/Mg	3.34
Selectivity coefficient A/Na	0.19
Selectivity coefficient A/K	–3.51
Organic pk_1	7.0
Organic pk_2	14.0
CO_2 partial pressure soil 0.0219	
CO_2 partial pressure stream 0.0011	
Stream Temperature °C	10.0
Base saturation 1990 %	9.25
Initial Base saturation 1850 %	12.56
Weathering rate, Ca	6.0
Weathering rate, Mg	6.0
Weathering rate, Na	0.0
Weathering rate, K	2.0
Nitrate uptake %	99.0
Ammonium uptake %	60.0
Soil Temperature °C	10.0

MAGIC simulation of Scoat, Greendale and Burnmoor Tarns

Prior to simulating acidification using MAGIC, it is necessary to estimate the deposition of dry inputs. Using the average rainfall chemistry data from 1983–1990 as the input of atmospheric deposition, an additional deposition factor of 1.1 was calculated by assuming chloride and sodium concentrations in Scoat Tarn are derived almost entirely from marine origin. This is supported by Sutcliffe and Carrick (1983) who found that chloride was derived from precipitation, evaporation, mist and dry deposition rather than from groundwater. It is also assumed that the background deposition inputs for 1850 are the same as that of sea salt concentration in present rainfall.

MAGIC has been set up for the three tarns assuming one dominant soil compartment through which the incoming water travels. The 140 year deposition history (1850–1990) was estimated for Scoat Tarn based on the historic sulphur dioxide emission records. The emission data used was those calculated by the Warren Spring Laboratory (Barrett *et al* 1983) and the records were extended to 1990 by assuming a 30% decrease in emissions from 1980 values. Figure 2 shows the sulphate deposition trajectory used in MAGIC. The deposition curve for the atmospheric pollution was assumed to have an identical shape to the regional emission data. This is a reasonable assumption as bulk deposition generally changes proportionally to changes in emissions (Warren Springs 1987). The trajectory for each ion that increased in concentration between 1850 and 1990 was scaled to the emission shape for use in the MAGIC model, as shown in Fig. 2.

An optimization procedure involving the use of MAGIC coupled to an optimization routine has been used to estimate weathering rates and background base saturation levels for MAGIC and Table 5 shows a parameter set optimization. A Rosenbrock hill climbing optimization routine is used to obtain an optimal parameter set.

The weathering rates estimated for Scoat Tarn are relatively low, reflecting the mineralogy of the catchment. The MAGIC lake chemistry output reproduces the observed chemistry of Scoat Tarn very closely as shown in Tables 4 and 6.

The historical pH values simulated by the model can be compared to those derived from the historical diatom analyses (Fig. 3). The model adequately simulates the historical change in acidity of Scoat Tarn and although differences exist, these are within the limits of measurement error. Figure 4a shows the alkalinity simulated by MAGIC over the same period, indicating a significant reduction from 1840 to the 1970s. The negative alkalinity reflects the acidic nature of the present system and

Table 6. Simulated Chemistry using MAGIC (all units $\mu g l^{-1}$ except pH)

	Scoat Tarn	Greendale	Burnmoor
Ca	42.5	48.7	43.8
Ma	39.8	48.6	69.2
Na	173.7	174.4	208.4
K	6.2	6.2	9.7
SO_4	62.5	63.1	73.7
Cl	213.2	213.0	216.0
pH	4.8	4.9	6.3

includes signs that a slight recovery in alkalinity has occurred in the 1980s, following the reduction in sulphate deposition. The process of soil acidification is of particular importance to the whole question of acidification and Figure 4b shows that soil base saturation % fell consistently over this period.

GREENDALE AND BURNMOOR TARNS

Similar MAGIC simulations for Greendale and Burnmoor Tarns are illustrated in Figures 5a and b, where pH trends from MAGIC compare well with the reconstructed trends from palaeoecological analysis. The major difference between the tarns is the non-acidic nature of Burnmoor compared with the acidic trends shown in Greendale and Scoat. The presence of glacial till in the Burnmoor Tarn catchment ensures a major supply of calcium ions which is reflected in the high calcium concentrations in the tarn (see Table 4). The soil survey shows much higher base saturations in the soils in Burnmoor and this has been incorporated into MAGIC, in addition to much higher weathering rates. As might be expected, sulphate reductions will have little effect on Burnmoor Tarn but results from Greendale Tarn are very similar to those of Scoat Tarn.

Impacts of future changes in sulphate and nitrate deposition

As sulphur reduction protocols have now been negotiated across Europe, the likely effects of sulphate deposition strategies adopted by the UK are of particular interest. Scenarios using MAGIC can, therefore, be run to assess the potential reversibility of lake acidification, assuming various levels of sulphur reduction in future rainfall and indicating future pH and alkalinity levels. Figures 6a and 6b show the predicted effects on pH and alkalinity for sulphate reductions from 30% to 90%. Only at the higher reduction levels is a sustainable pH recovery simulated and a zero alkalinity achieved within a reasonable

(a)

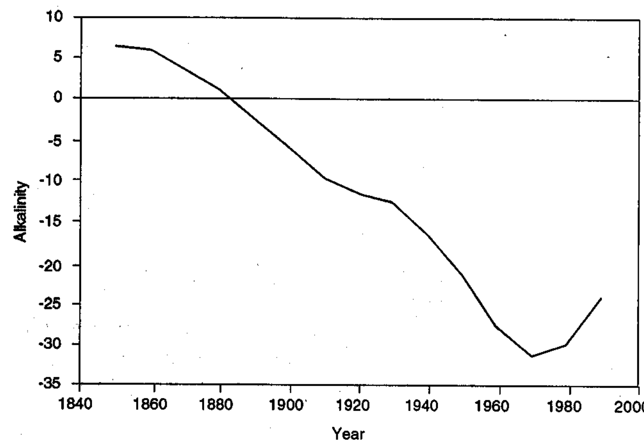

Figure 4a: MAGIC simulated lake alkalinity for Scoat Tarn

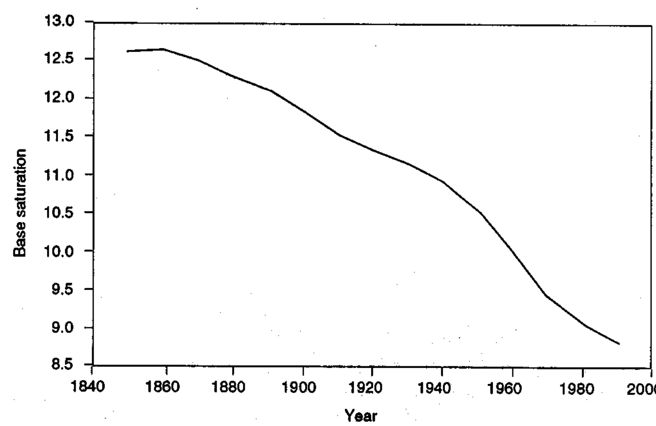

Fig. 4 *(a) MAGIC simulated lake alkalinity for Scoat Tarn (b) MAGIC simulated base saturation % for soils in Scoat Tarn catchment*

timescale. Scoat Tarn is included in the DOE Acid Waters Monitoring Network (Patrick, *et al.*, 1995) and there are no signs that recovery is underway yet. However, as indicated by the MAGIC simulation, this is not surprising given the long history of acid deposition and the slow recovery predicted by the model.

Of increasing concern is the rising levels of nitrogen in the environment and, in particular, the increasing concentrations of nitrate in rainfall and the atmosphere. The DOE INDITE Report (1993) gives a comprehensive review of nitrogen processes and predicts increasing levels of nitrogen given the rising trends in vehicle emissions. Nitrogen is included in MAGIC and it is possible to simulate the combined effect of a sulphate reduction coupled to a nitrate increase in the future. A realistic simulation is to assume that this 25% increase in nitrate happens in parallel with an 80% reduction in sulphate. Figure 7 shows the combined effect of sulphate reduction and nitrate increases and recovery is not as rapid as with sulphate alone. This is to be expected, given that

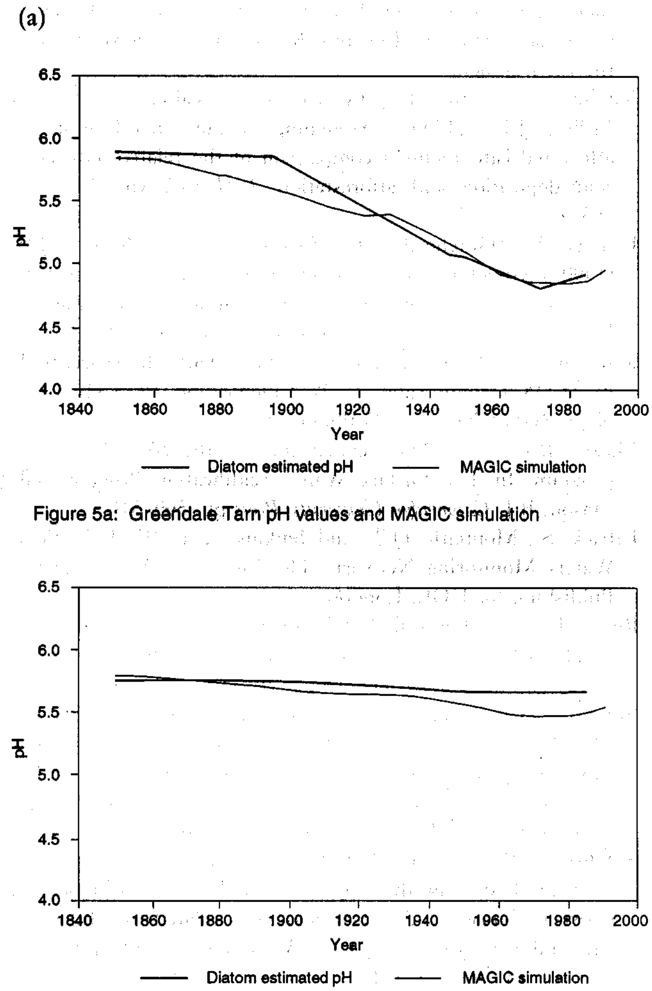

Fig. 5 *(a) Greendale Tarn pH values and MAGIC simulation (b) Nurnmoor Tarn pH values and MAGIC simulation*

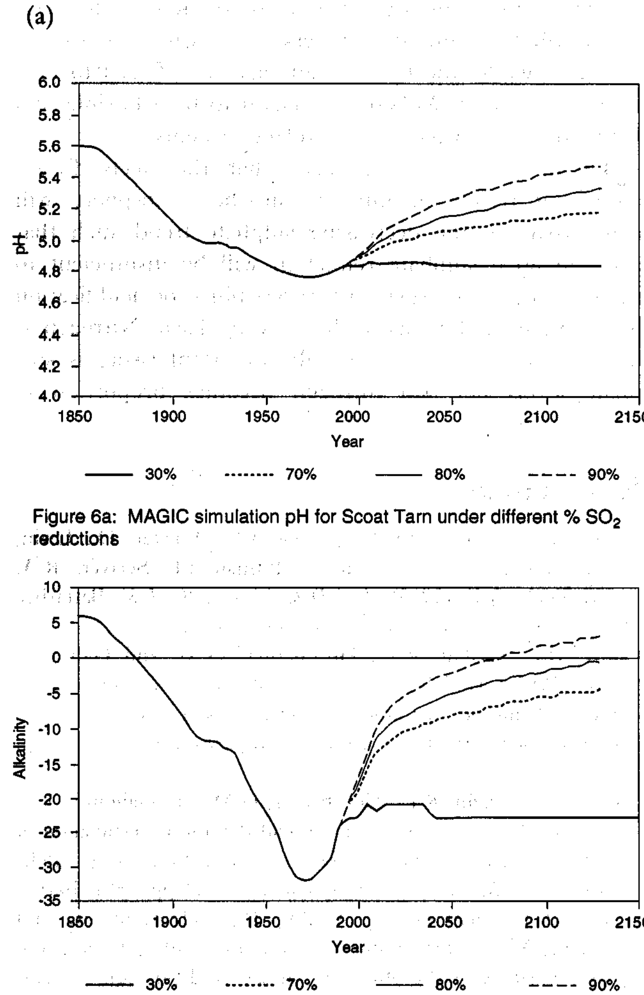

Fig. 6 *(a) MAGIC simulation pH for Scoat Tarn under different % SO_2 reductions (b) MAGIC simulation lake alkalinity for Scoat Tarn different % SO_2 reductions*

both sulphate and nitrate act as strong acid anions. It should be emphasized that this nitrogen simulation effect contains few process mechanisms except anion-cation exchange and plant uptake. Improvements to MAGIC include additional nitrogen processes and these are described by Ferrier *et al* (1995). Even this enhanced version of MAGIC does not take into account all of the processes known to affect nitrogen and Whitehead (1997) describes an integrated process-based model of nitrogen for catchments that does take into account all the key processes. Nevertheless, the simulation results presented here give a realistic assessment of the likely impacts of nitrogen on the Lake District Tarns.

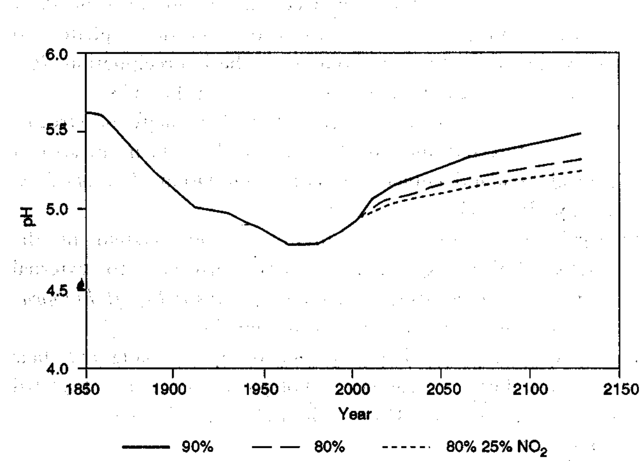

Fig. 7 *MAGIC simulation for different scenarios of SO_2 reductions and one simulation for an increase of NO_2 of 25% by 2020 with an 80% reduction in SO_2*

Conclusions

The MAGIC model has been applied successfully to the three Lake District Tarns and has been used to indicate likely future responses under different deposition scenarios. These indicate that major reductions in deposition will be required to reverse acidification in two of the tarns whilst the third is sufficiently buffered to prevent acidification. MAGIC is shown to be a flexible tool for modelling acidification in upland systems.

There is, however, concern that the likely future increasing trends in nitrogen in the atmosphere will counterbalance the decreasing sulphate trend such that even an 80% sulphate reduction will be insufficient to achieve long term sustained reversibility of acidification in sensitive catchments such as Scoat Tarn. Nitrogen is likely to become an increasingly important issue, as sulphate levels fall and nitrogen becomes proportionally more important.

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